

## Micelles, Vesicles and Microemulsions

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A theory of self-assembly of surfactant molecules into micelles and bilayers is critically examined and extended to include vesicles and microemulsions. The notion of hydrophilic-lipophilic balance is quantified. The theory gives a unified account of type, size and shape of the aggregates which form under various conditions. Observed trends due to change in salt concentration, temperature and oil type, and due to the addition of cosurfactants, are correlated and emerge from a simple global framework.

### 1. INTRODUCTION

Until a few years ago the possibility that all observations on association colloid systems could ultimately be handled by a single theoretical framework seemed remote. It became less so following attempts<sup>1,2</sup> to extend the ideas of Tanford<sup>3</sup> and others<sup>4</sup> on dilute micellar aggregates to larger surfactant associations like cylindrical micelles, vesicles and bilayers. The main point of departure lay in quantifying the part played by molecular geometry (packing) in determining allowed structures. It was an old idea<sup>5</sup> which had been allowed to lie fallow. And it worked. Theory does appear to be on the right track. While there are gaps, parts of the jigsaw puzzle have been filled in more or less satisfactorily for dilute surfactant solutions. Certainly many of the physical properties of micelles and vesicles like size, shape, c.m.c. and polydispersity appear to be accessible without a detailed knowledge of the complex intermolecular forces involved.

Our purpose here is twofold: (1) To attempt to define better and explore some of the basic assumptions which underlie ideas presently extant. (2) To see how these ideas might be extended to include multicomponent systems (microemulsions).

From a pragmatic point of view, one main aim of studies in the subject must surely be: to elucidate the phase diagrams of water-surfactant (and cosurfactant)-hydrocarbon mixtures; in particular to identify which structures form, when and why; and as a corollary: how to maximise solubilisation of oil in water, or water in oil, with a minimum surfactant (cosurfactant) concentration.

This aim is ambitious, and the problem of such complexity that, to paraphrase and borrow a remark made by Stillinger:<sup>6</sup> "it is essential to maintain a respectable balance between the sterile intricacy of formal theory and the seductive simplicity of poetic 'explanation'". Before beginning our study it may be useful to expand this dictum. In attempting to make a theory there are two extreme approaches. A fundamental treatment using statistical mechanics which takes into account complex surfactant molecule interactions in water is possible in principle. However, even the hydrophobic interaction between two small molecules in water is still a matter of dispute.<sup>7</sup> Further, the simplest prototype for aggregation, the problem of nucleation (and consequent phase transition) in a van der Waals gas, is an open subject. Moreover, the high road *via* statistical mechanics is necessarily so complicated that physical insight tends to be wholly obscured.

At the other end of the spectrum one can avoid detailed models as far as possible and search for a unified thermodynamic picture like that of Tanford,<sup>3</sup> and of Israelachvili *et al.*<sup>1</sup> for micelle and bilayer formation. But thermodynamics is tautological and can go so far. At a certain point *some* details of molecular interaction must be invoked. Our guiding principle in attempting to steer a middle course between these two extremes will be that these details must be minimal. Otherwise, with too many (unknown) parameters, theory tends to become an exercise in curve fitting, a numerical game which loses predictive capacity and credibility.

An immediate consequence is that language must be used with some care. The problem is here doubly compounded and confounded by the fact that words like amphiphile, hydrophobic, hydrophilic, lipophilic, aggregate, micelle, are either anthropomorphic in origin (disguising their complexity) or intuitive, ill-defined, and are so familiar that we tend not to question their meaning. This question of definitions will plague us throughout and is unavoidable. A result is that our essay has elements of schizophrenia, with necessary appeal to formal statistical mechanics (relegated to an appendix) interspersed with (hopefully) an occasional insight gleaned from intuition and simple models.

## 2. THERMODYNAMICS OF DILUTE SOLUTIONS OF SURFACTANTS

Dilute micellar systems have been the subject of an extensive literature which we do not wish to recapitulate in detail. Given certain "reasonable" assumptions they are broadly speaking understood. However, conflicting opinion on questions like the stability of vesicles and the delicacy of experiments on microemulsions, to name two areas of many, will demand re-examination of foundations as we proceed.

For the moment it suffices to assert that a dilute solution of surfactant molecules can be considered to consist of solvent plus monomers, dimers, trimers, . . . and larger allowed aggregates (micelles, vesicles, liposomes, . . .). The concentration is assumed to be so low that aggregates can be considered to be non-interacting. The distribution of aggregates is then determined by the law of mass action, eqn (1),

$$\mu_N^\circ + \frac{kT}{N} \ln \left( \frac{X_N}{N} \right) = \mu_1^\circ + kT \ln X_1, \quad (1)$$

where the chemical potential of an aggregate of size  $N$  has been written as  $N\mu_N^\circ + kT \ln (X_N/N)$  and  $X_N$  is the concentration (mole fraction, volume fraction, . . .) of surfactant molecules in the  $N$ -aggregate. The theory also allows for the possible formation of infinite aggregates, *i.e.* separate phases, a problem which we defer. The glib assertion eqn (1) represents a beginning to a chemist and an essential stumbling block to a physicist who can go no further without questioning origins. If aggregates of a given  $N$  were distinct, identical well-defined *chemical* species there would be no problem, apart from the vexed question of concentration units. They are not: even within a given  $N$ -aggregate, if such can be defined, there exist an infinite diversity of conceivable shapes or configurations which the association of surfactant molecules could take up. Implicit in eqn (1) is the understanding that for any  $N$  a shape of minimum energy exists and is overwhelmingly more probable than its fellows. These problems are addressed in the Appendix. If the arguments there advanced are accepted we return to eqn (1) which can be rewritten in the form

$$\frac{X_N}{N} = X_1^N \exp \left[ -N(\mu_N^\circ - \mu_1^\circ)/kT \right]. \quad (2)$$

All aggregates can occur at any concentration, albeit with infinitesimal probability even below the critical micelle concentration (c.m.c.). Above the c.m.c., defined by  $X_1 = \sum_{N>1} X_N$ ,  $X_1$  increases slowly with concentration. It is shown in ref. (1) that if  $\mu_N^\circ$  is sharply distributed about some  $N$  then the distribution of aggregates peaks at a value of  $N$  just less than the  $N$  with minimum  $\mu_N^\circ$  and is also sharply distributed. Otherwise pronounced polydispersity may occur (e.g. for long, cylindrical micelles). Thus reduced to bare bones, it can be seen that the use of the word "theory" is dubious. We have simply characterized the observation of micelles, and have shown *via* the Appendix that the law of mass action is an appropriate vehicle for this characterisation.

The entropic term  $(kT/N) \ln (X_N/N)$  in eqn (1) has considerable nuisance value. For that reason it will usually be helpful in dealing with finite aggregates to adopt a simpler basis for our subsequent development. This is the so-called pseudophase approximation wherein one drops the entropic term. In the pseudophase approximation no micelles occur below the c.m.c. (This is now the value  $X_1$  of monomer concentration for which  $\mu_N^\circ = \mu_1^\circ + kT \ln X_1$ .) Above this c.m.c. all additional surfactant molecules form micelles or whatever aggregate has the minimum  $\mu_N^\circ$ . No other aggregates form until activity coefficients, i.e. interactions between aggregates, become significant. Keeping in mind possible complications due to phase transitions and interactions the strategy is then to compare the chemical potentials of different aggregates to see which has the minimum  $\mu_N^\circ$ .

#### THE FORM OF $\mu_N^\circ$

In essence the simplest version of current theory<sup>1</sup> assumes a form

$$\mu_N^\circ = \mu_N^B + \mu_N^S + \mu_N^C + \text{"packing term"} \quad (3)$$

= "bulk term" + "surface term" + "curvature term" + "packing".

Its decomposition is as follows (cf. fig. 1).

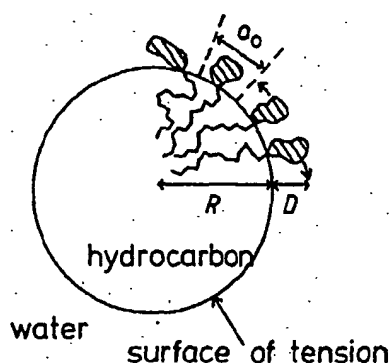


FIG. 1.—Schematic representation of model spherical micelle of radius  $R$ .

**Bulk Term:** This is a constant term, the same for all aggregates, which measures the hydrophobic free energy of removing hydrocarbon tails from water into an assumed oil-like phase made up of all tails which form the micelle interior. The interior is assumed to be fluid in estimating this free energy transfer.

**Surface Term:** This includes a term<sup>†</sup>  $\gamma a$  to allow for the fact that hydrophobic tails still have some contact with water, where  $a$  is the area per surfactant molecule, and  $\gamma$  is an interfacial tension.

<sup>†</sup> It is a trivial decoration to exclude that fraction of the "oil"-water interface taken up by head groups.

Opposing this attractive energy is a term to account for repulsive head-group interactions. These interactions can be due to steric repulsion, hydration, electrostatic and other forces. They are not yet quantified. If electrostatic in origin the simplest phenomenological description would give a term  $\propto 1/a$ . The total surface contribution would then be written

$$\mu_N^s = \gamma \left( a + \frac{a_0^2}{a} \right) \quad (4)$$

which takes its minimum value  $2\gamma a_0$  at an optimal area  $a_0$  per head group. This form for the repulsive contributions to  $\mu_N^s$  cannot be taken literally, and its precise form is immaterial. Any mathematical description of the surface contributions which recognises that several competing forces will lead to an optimal area  $a_0$  per head group will lead to the same conclusions.

**Curvature Term:** If as an aid to analysing data on ionic micellar solutions we were to persist with an electrostatic model for head-group repulsions,<sup>1</sup> then for a curved, rather than planar, surface the term  $a$  in  $\gamma a_0^2/a$  would be replaced by  $a(1 + D/R)$  where  $R$  is the mean radius of curvature and  $D$  the Debye length. An alternative way of visualising a mechanism for curvature effects is to imagine that the centre of action for head-group repulsion is displaced a distance  $D$  from the "oil"-water interface. Then  $a$  would be replaced by  $a(1 + D/R)^2$ . We choose the first form again only to have some plausible mathematical realisation of the undoubted existence of curvature energy.

**Packing Term:** The assumption that the interior of an aggregate is fluid-like and is to a first approximation incompressible has an immediate consequence, provided we admit that aggregates can obtain no holes. [The occurrence of an interior vacuum of water-filled region inside the (oil-like) interior of an aggregate would result in a large unfavourable increase in free energy, which possibility is excluded from consideration].<sup>†</sup> This can be taken into account if we assume  $\mu_N^s = \infty$ , hence a packing criterion is violated. For spherical and cylindrical micelles this criterion is  $R < l_c$  where  $l_c$  is a critical tail-length which in ref. (1) was taken to be ca. 80–90% of the fully extended chain length for bilayers. The packing criterion is clearly an extreme, albeit useful, oversimplification. We shall see later that it can, and indeed must be relaxed. The melding of the two notions, of a fluid-like interior for the micelle and of "packing", is at first sight contradictory. However, the two notions can be shown to be compatible in a first-order theory.<sup>8</sup>

In addition to the contributions above to  $\mu_N^s$  there will be others with increasing concentration due to interactions.

### 3. GEOMETRICAL CONSIDERATIONS AND ZERO-ORDER THEORY

Possible candidates for aggregates can now be examined. For surfactant-water systems these are spherical micelles, non-spherical micelles (globular and cylindrical), vesicles, liposomes, bilayers, and for oil-surfactant-water systems spherical drops, normal or inverted (water dispersed or oil dispersed, respectively). We assume that the surfactant molecule can be divided unambiguously into a head group and tail and that the partial volume  $v$  of the tail is prescribed so that for an aggregate of number  $N$  the tail region volume is  $Nv$ .

The location of the interface which defines the radius  $R$  is a difficult question with different conventions adopted by different authors.<sup>1,9</sup> However if the theory is *not* to

<sup>†</sup> Note added in proof: Experimental observations which have sometimes been interpreted as implying water penetration in the hydrophobic core of micelles are completely explicable in terms of the sampling of the surface groups in the chains (D. W. R. Gruen, to be published).

depend on specific details, the convention must also not be critical. Take the interface to be the surface which bounds the volume occupied by hydrocarbon tails. Then for spherical micelles (fig. 1) we have  $\frac{4}{3}\pi R^3 = Nv$  and a head-group area defined by  $4\pi R^2 = Na$ . The packing criterion imposes the condition that the average chain length is  $R \leq l_c$ .

By zeroth-order theory we mean one in which  $a \approx a_0$ , the optimum area for a bilayer, independent of the size and shape of the micelle. (Head-group curvature is assumed to be a small perturbation.) Because the zeroth-order theory prescribes  $a = a_0$ , the dimensions of the spherical micelle are completely determined ( $R = 3v/a_0$ ), i.e.  $R > l_c$ . Then if  $v/a_0 l_c > \frac{1}{3}$ , "the optimum-energy spherical micelle" is disallowed by packing because then  $R > l_c$ . On the other hand, for  $R \leq l_c$  spherical micelles allowed by packing are energetically disfavoured (because  $a > a_0$ ). In higher-order theories  $a$  will be determined by optimisation of  $\mu_N^\circ$  and the optimum spherical micelle ( $R \leq l_c$ ) will be compared with other shaped aggregates.

Problems of packing are extremely complex for shapes of low symmetry. For shapes of high symmetry the packing criterion is easy to visualise. In other cases the simplest condition is that no interior point can be less than a distance  $l_c$  from the surface. This criterion leads to the conclusion that only oblate shapes should occur.<sup>1,10</sup> In practice this is not so, and large prolate or rod-shaped micelles are observed.<sup>1,28</sup>

To overcome this difficulty in ref. (1) the authors imposed a plausible restricted (local) packing criterion. As there shown, the pseudophase approximation breaks down, and large polydisperse cylindrical micelles form. Their size distribution depends on concentration. So as not to distract from our main theme it will be sufficient to treat non-spherical micelles as if they were infinite cylinders. For cylinders  $R = 2v/a_0$  so that packing requires  $v/a_0 l_c < \frac{1}{2}$ .

So far for  $v/a_0 l_c < \frac{1}{3}$ , the zeroth-order theory admits either a sphere or a cylinder. To determine which is the favoured aggregate we can have recourse to two arguments. In ref. (1) appeal was made to translation entropy which favours the smallest aggregate, i.e. a sphere. However, we can invoke the head-group curvature energy which also prefers the sphere because of its greater curvature.

Note that micelles are forbidden for  $v/a_0 l_c > \frac{1}{2}$ . In this region we have to search for different allowed structures. These could be, e.g., vesicles, liposomes or multilamellar aggregates. For the moment consider only vesicles and single bilayers. In discriminating between these, the head-group curvature again favours the smallest aggregates as does entropy, i.e. the smallest vesicle allowed by packing is preferred.

The zeroth-order theory also allows vesicles for  $v/a_0 l_c < \frac{1}{2}$ . However, it will be shown in section 4 that the preferred vesicles have physically absurd internal parameters which necessitate the imposition of a further packing constraint. Once this is taken into account cylinders become the energetically favoured structures for  $\frac{1}{3} < v/a_0 l_c < \frac{1}{2}$ .

With this proviso, the overall prediction is that we obtain

spherical micelles	$v/a_0 l_c < \frac{1}{3}$	
cylindrical micelles	$\frac{1}{3} < v/a_0 l_c < \frac{1}{2}$	
bilayers (or vesicles)	$\frac{1}{2} < v/a_0 l_c < 1$	(5)
inverted structures	$v/a_0 l_c > 1$	

Apart from the question of internal packing alluded to above, there are other problems with this theory which require detailed examination: We have no reason to assume that curvature effects due to head-group interactions are necessarily small, in the sense of a perturbation. If they become large, the zeroth-order theory breaks down in any event because the head-group area may no longer be fixed to first

approximation as equal to that for a (planar) bilayer. We have no reason to assume that curvature is predominantly due to head-group interactions. There may well be curvature effects due to hydrocarbon tails of comparable magnitude which could even take a different sign (vesicle-forming surfactants generally have relatively large hydrocarbon volumes).

In addition the experimental situation is still unresolved. Some authors<sup>11-13</sup> believe that vesicles are thermodynamically unstable (the stable state being the lamellar phase). Monodisperse vesicles of size given by the zeroth-order theory<sup>2</sup> can be produced through prolonged sonication. This is generally taken to indicate that energy is required for their production. When monodisperse vesicles are so produced and cooled below the gel temperature, they become unstable and grow in size, eventually forming lamellar particles.<sup>13</sup> On reheating, whatever size distribution existed at the lower temperature is apparently "frozen" and seems to be kinetically stable.<sup>13,14</sup> Again it is claimed that with other preparation techniques any size vesicle can be made to order.<sup>15</sup> Not all these different distributions of vesicles can be the thermodynamically stable state. All that can be inferred is that vesicle dispersions are very slow to equilibrate, so that it is difficult to ascertain the equilibrium situation.

On the other hand, on addition of excess water, the lamellar phase disperses spontaneously to form multilamellar particles or liposomes<sup>16,17</sup> (e.g. lecithin) or vesicles<sup>17,18</sup> (e.g. phosphatidyl serine). This would seem to suggest that the lamellar phase may not be stable in a dilute solution.

Another problem which we have not yet addressed is that of interactions between bilayers. The question of stability of vesicles cannot be resolved theoretically without proper account of interactions. For all these reasons the problem of vesicles needs to be reconsidered with care.

## 4. VESICLES

### 4.1 PACKING IN VESICLES

We consider first consequences of packing conditions which apply under the assumptions of (1) constant volume  $v$  per surfactant molecule and (2) constant head-group area  $a_0$  for a surfactant molecule. In general a vesicle (cf. fig. 2) of aggregation number  $N$  is described by four parameters of the set  $v, a_e, a_i, l_e, l_i, R_e, R_i, N, N_e, N_i$ , where the subscripts  $e, i$  refer to external and internal parameters. Of these we take the first four  $v, a_e = a_i = a_0, l_e$  to be given. We have

$$\frac{4\pi}{3}(R_e^3 - R_m^3) = N_e v, \quad 4\pi R_e^2 = N_e a_0, \quad R_e - R_m = l_e \quad (6)$$

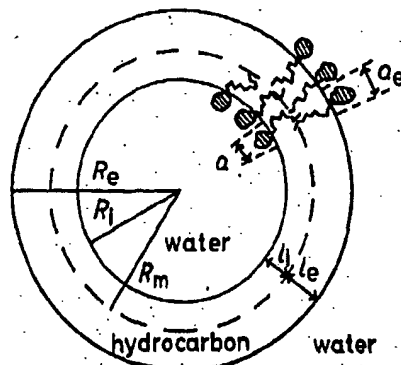


FIG. 2.—Geometry of a model vesicle.

whence

$$\frac{l_e}{R_e} = \frac{3}{2} - \sqrt{\frac{3v}{a_0 l_e} - \frac{3}{4}}, \quad \frac{1}{3} < \frac{v}{a_0 l_e} < 1. \quad (7)$$

As  $v/a_0 l_e$  increases from  $\frac{1}{3}$  to 1,  $R_e/l_e$  increases from 1 to  $\infty$ , and  $R_e$  increases from  $3v/a_0$  to  $\infty$ . Hence for fixed  $v, a_0$  the smallest vesicle is given by the largest  $l_e$ . Thus, since  $l_e \leq l_c$ , the smallest vesicle corresponds to  $l_e = l_c$  (provided  $v/a_0 l_c > \frac{1}{3}$ ).

In the following we determine the dimensions of the vesicles as a function of the simple parameter  $v/a_0 l_e$ . The numbers listed in table 1 follow from the relations eqn (6) and (7) and the further conditions

$$\frac{4\pi}{3}(R_e^2 - R_i^2) = Nv, \quad 4\pi(R_e^2 + R_i^2) = Na_0 \quad (8)$$

whence if  $x = R_i/R_e$ ,  $y = 3v/(a_0 R_e)$

$$\frac{1-x^3}{1+x^2} = y, \quad 0 < x, y < 1. \quad (9)$$

Formally the model allows vesicles (with  $l_e = l_c$ ) for  $v/a_0 l_c > \frac{1}{3}$ . However, as can be seen from table 1, in practice for  $\frac{1}{3} < v/a_0 l_c < \frac{1}{2}$  these vesicles are excluded. In this region the number of surfactant molecules "packed" on the inside of an optimum vesicle is less than a whole number, which is inane. Clearly some additional packing criterion must be invoked since the values of  $l_i$  for the mean length of internal chains are ridiculously small for  $v/a_0 l_e < \frac{1}{2}$ . Within the framework of our zeroth-order theory (fixed head-group area) this condition would have the form  $l_i \geq \alpha l_e$ ,  $0 < \alpha < 1$  where  $\alpha$  is a parameter ultimately related to details of chain-chain interactions. At the very worst we must have  $l_i > 2-3 \text{ \AA}$  say, roughly the length of a  $\text{CH}_2$  bond. Assume that such a condition is invoked. Then the smallest vesicle allowed by packing in the range  $\frac{1}{3} < v/a_0 l_c < \frac{1}{2}$  will correspond to some  $l_e$ ,  $\frac{1}{2} < v/a_0 l_e < 1$ . Depending on internal packing constraints, i.e. the value of  $\alpha$ , such vesicles may have small aggregation numbers. Thus if entropy was the sole deciding factor, vesicles would *always* be favoured over the large cylindrical micelles observed in practice. [As shown in ref. (1) cylindrical micelles once formed tend to grow without limit.] Therefore another factor must decide the issue. We now show that once curvature energy, however small, is taken into account cylinders are almost certainly always energetically favoured over vesicles in the range  $\frac{1}{3} < v/a_0 l_c \leq \frac{1}{2}$ .

#### 4.2 CYLINDERS vs. VESICLES

Plausible simple forms which take account of curvature energies due to head-group repulsion have been alluded to in section 2. These will be discussed further below (section 4.3) and are clearly model-dependent. Thus an electrostatic model for the surface contribution to  $\mu_N^s$  [eqn (3)] would replace the term  $\gamma a_0^2/a$  for a planar aggregate by  $\gamma a_0^2/a(1 + D_1/R)$  for a spherical aggregate. A different model which recognised head-group size would replace this term by  $\gamma a_0^2/a(1 + D_2/R)^2$ . However, provided curvature represents a *weak* perturbation, linearisation is allowed. All models then lead to the same approximate form  $\gamma(a_0^2/a)[1 - D/R]$  where  $1/R = \frac{1}{2}[(1/R_1) + (1/R_2)]$ ,  $R_1$  and  $R_2$  being the principal radii of curvature of the aggregate, and  $D$  is some unknown constant characteristic of a given surfactant. If curvature due to head-group interactions dominates over chains, which is implicit in our zeroth-order theory,  $D$  must be positive for a convex surface and negative for a

TABLE 1.—DIMENSIONS OF VESICLES IN ZERO-ORDER THEORY

$v/a_0 l_e$	$R_e/l_e$	$R_i/l_e$	$(R_m - R_i)/l_e$	$R_e/\text{\AA}$	$R_i/\text{\AA}$	$l_e = 20 \text{\AA}$ $l_i = (R_m - R_i)/\text{\AA}$	$(R_e - R_i)/\text{\AA}$	$a_0 = 60 \text{\AA}^2$ $N_i$	$N_e$	$N$
0.333	1	0	0	20	0	0	20	0	83	83
0.35	1.05	0.01	0.04	21	0.2	0.8	20.8	0.01	92	92
0.4	1.21	0.08	0.12	24	1.7	2.5	22.3	0.6	120	121
0.5	1.56	0.32	0.25	31.5	6.5	5.1	26.4	8.8	208	210
0.6	2.1	0.73	0.37	42	14.6	7.5	27.5	44	369	413
0.7	2.96	1.45	0.50	59	29	10	30.1	176	729	905
0.8	4.64	3.00	0.65	93	80	13	33.0	753	1811	2565
0.85	6.3	4.59	0.73	126	92	14.6	34.6	1800	3300	5100
0.9	9.65	7.84	0.81	193	157	16.3	38.3	5200	7800	12900
0.95	19.7	17.7	0.9	393	355	18	38.1	26000	32200	59000
1	$\infty$	$\infty$	1	$\infty$	$\infty$	20	40	$\infty$	$\infty$	$\infty$

Dimensions of vesicles based on putting  $a = a_0$ . First three columns are scaled, i.e. hold for all  $v/a_0 l_e$ . Last three are explicit for  $l_e = 20 \text{\AA}$ ,  $a_0 = 60 \text{\AA}^2$ . (For egg lecithin,  $l_e \approx 17.5 \text{\AA}$ .) Note that the same packing conditions apply to microemulsions which begin, in the sense that  $V_{oil} = V_{surfactant}$ , i.e.  $R_e^3 = \frac{1}{2} R_i^3$ , at ca.  $v/a_0 l_e = 0.8$ .



concave surface. We now compare the energies of cylinders and vesicles (with the same  $v$  and  $a_0$ ). For cylinders we have

$$\mu_N^S(\text{cylinder}) = \gamma \left[ a + \frac{a_0^2}{a} \left( 1 - \frac{D}{2R_c} \right) \right] = 2a_0\gamma - \frac{Da_0\gamma}{2R_c}; \quad R_c = \frac{v}{2a_0} \quad (10)$$

where  $R_c$  is radius of the cylinder. By contrast, for vesicles we have

$$\mu_N^S(\text{vesicle}) = \frac{N_e \mu_e^S + N_i \mu_i^S}{N} \quad (11)$$

where

$$\begin{aligned} \mu_e^S &= \gamma \left[ a_e + \frac{a_0^2}{a_e} \left( 1 - \frac{D}{R_e} \right) \right] = 2\gamma a_0 - \frac{Da_0\gamma}{R_e} \\ \mu_i^S &= \gamma \left[ a_i + \frac{a_0^2}{a_i} \left( 1 + \frac{D}{R_i} \right) \right] = 2\gamma a_0 + \frac{Da_0\gamma}{R_i} \end{aligned} \quad (12)$$

Hence  $\mu^S(\text{vesicle})$  can be written

$$\mu^S(\text{ves})/\gamma = 2a_0 - \frac{Da_0}{N} \left( \frac{N_e}{R_e} - \frac{N_i}{R_i} \right) = 2a_0 - \frac{3Dv}{(R_e^2 + R_e R_i + R_i^2)} \quad (13)$$

where the last form follows from elementary geometry. Comparison of eqn (10) and (13) shows that cylinders will be energetically favoured over vesicles if and only if

$$\frac{1}{3}(R_e^2 + R_e R_i + R_i^2) > \left( \frac{2v}{a_0} \right)^2; \quad \text{or} \quad \frac{R_e^2 + R_i^2}{R_e - R_i} > \frac{4v}{a_0} \quad (14)$$

We now establish conditions under which the inequality holds. To do this we write  $r_e \equiv R_e/l_e$ ,  $r_i \equiv R_i/l_e$ ,  $x \equiv R_e/R_i$  so that the inequality (14) becomes

$$\frac{r_e^2 + r_i^2}{r_e - r_i} > \frac{4v}{a_0 l_e} \quad \text{or} \quad \frac{1 + x^2}{1 - x^2} > \frac{4v}{a_0 l_e} \quad (15)$$

Now  $r_e$ ,  $r_i$  and  $x$  are all functions of  $v/a_0 l_e$ . In fact from eqn (7)

$$\frac{1}{r_e} = \left( \frac{3}{2} - \sqrt{\frac{3v}{a_0 l_e} - \frac{3}{4}} \right) \quad (16)$$

and  $x$  is determined by eqn (9). Hence the condition eqn (15) can also be written as

$$\frac{(1+x^2)^2}{(1-x)(1-x^3)} > \frac{4}{3} \quad (17)$$

The solution of

$$\frac{(1-x)(1-x^3)}{(1+x^2)^2} = \frac{3}{4}$$

then determines vesicle parameters for which the inequality is satisfied. The required root is  $x = 0.1896$ , corresponding to which value we have from eqn (9) and (16)  $v/a_0 l_e = 0.4883$ ,  $v/a_0 l_i = 2.104$ ,  $R_e/l_e = 1.528$ ,  $R_i/l_e = 0.289$ ,  $l_i/l_e = 0.232$ . Therefore, vesicles which satisfy the conditions

$$\frac{v}{a_0 l_e} > 0.4883 \quad \text{or equivalently} \quad \frac{v}{a_0 l_i} < 2.104 \quad \text{or} \quad \frac{l_i}{l_e} > 0.2321 \quad (18)$$

will be energetically less favoured than the cylinder.

We now show that all vesicles satisfy this condition given the minimal packing condition of section 4.1. If  $v/a_0l_c > 0.4883$  the condition is satisfied since  $l_e \leq l_c$ . This is not a particularly interesting result since we know that cylinders are forbidden by packing in any case for  $v/a_0l_c > 0.5$ . On the other hand if  $v/a_0l_c < 0.4883$ , the external packing condition  $l_e \leq l_c$  is not sufficient to discriminate, and a packing condition on internal chains [cf. eqn (18)] is required. Let us impose the requirement  $l_i/l_c > 0.2321$ . Then certainly  $l_i/l_c > 0.2321$ . Thus for  $v/a_0l_c < 0.4883$ , the condition  $l_i/l_c > 0.2321$  is sufficient to ensure that cylinders are again the favoured structure. Typically for a lipid of  $l_c \approx 20 \text{ \AA}$ , the mean internal chain length of a vesicle which has an energy equal to the allowed cylindrical structure would be as low as  $4.6 \text{ \AA}$ . This is improbable. The corresponding vesicle would be an absurd structure, with aggregation number  $N \approx 26$ ,  $N_1 \approx 2$ .

To sum up: Within a framework which admits the zeroth-order theory as a first approximation, i.e. provided curvature is a perturbation, cylinders are always the favoured structure for  $\frac{1}{3} < v/a_0l_c < \frac{1}{2}$ . The imposition of a weak packing criterion on inside chains is necessary. This criterion cannot be spelt out precisely without a theory of chain interactions presently not available. However, the very strong requirement  $l_i > 0.232l_c$  appears to be eminently reasonable. Entropy which favours the smaller vesicles over cylinders has been ruled out as a major factor and curvature always dominates. (To quantify this conclusion roughly compare the entropic contribution to  $\mu_N$  of eqn (1) with curvature energies. Take  $X_N = 1$  as an extreme upper bound. Then even for a small vesicle  $N \geq 500$ ,  $R_e \approx 50 \text{ \AA}$ ,  $\gamma \approx 50$ ,

$$\left| \frac{kT}{N} \ln \left( \frac{X_N}{N} \right) \right| \approx 10^{-2} kT.$$

For  $D$  as small as  $1 \text{ \AA}$ , the smallest possible characteristic length which has much meaning, the curvature contribution to  $\mu_N$  would be [cf. eqn (13)]  $> 4Dv/R_e \approx 20 \times 10^{-2} kT$ .)

## 5. FURTHER CONSIDERATIONS ON VESICLES— NON-LINEAR EXTENSIONS

### 5.1 VESICLES *vs.* BILAYERS

The zeroth-order theory of section 4.1 suggests that vesicles would be the preferred structure in the range  $\frac{1}{2} < v/a_0l_c < 1$ . However, we have shown that the weak packing criterion for hydrocarbon chains  $l_e < l_c$  is not sufficient. Recognition of the role of an internal packing constraint can dramatically alter the picture. We first investigate vesicle parameters in the zeroth-order approximation with the constraint  $l_i > \alpha l_c$ . The strong condition  $l_i \geq 0.25 l_c$  established in section 4.2 provides one bound on  $\alpha$ . Evidence from multilayer studies suggests that the upper bound on  $\alpha$ ,  $\alpha \leq 0.5$ , is a reasonable guess.<sup>19</sup> Vesicle parameters for  $\alpha = 0.5$  are listed in table 2. These results were obtained numerically by solution of eqn (6)–(9) with the additional constraint  $l_i > \alpha l_c$ .

Note that for  $\alpha = 0.5$ , as  $v/a_0l_c$  decreases from unity (bilayer formation favoured) vesicle size diminishes to around  $v/a_0l_c = 0.7$ . Thereafter the optimal vesicle size increases until at  $v/a_0l_c = \alpha = 0.5$  bilayers are again the favoured structure. The turning point can be read off from table 1. Thus if

$$\frac{l_i}{l_c} = \frac{R_m - R_l}{l_0} = 0.65$$

TABLE 2.—EFFECT OF INTERNAL PACKING CONSTRAINTS ON VESICLES WHEN  
 $a = a_0$ ,  $\alpha = 0.5$ ,  $v = 1063 \text{ \AA}^3$ ,  $l_c = 20 \text{ \AA}$ 

$v/a_0 l_c$	$a_0/\text{\AA}^2$	$R_c/\text{\AA}$	$R_l/\text{\AA}$	$l_c/\text{\AA}$	$l_l/\text{\AA}$	$N_c$	$N_l$
(1.0)	53	$\infty$	$\infty$	20	20	$\infty$	$\infty$
(0.97)	54.5	793	700	20	18.9	125 600	112 700
(0.87)	61	143	108	20	15	4 200	2 400
(0.79)	68	88	55	20	12.5	1 430	560
(0.74)	72	66	36	20	10.8	760	220
(0.69)	77	58	28	20	10	560	130
(0.65)	82	61	33	18	10	580	170
(0.59)	90	79	54	14.3	10	880	420
(0.56)	94.5	98	76	13	10	1 300	770
(0.54)	98	137	115	11.9	10	2 430	1 720
(0.50)	106	$\infty$	$\infty$	10	10	$\infty$	$\infty$

Vesicle parameters with  $v = 1063 \text{ \AA}^3$  (corresponding to egg lecithin<sup>1</sup>) and  $l_c$  taken to be  $20 \text{ \AA}$ , with varying head-group area  $a_0$ .  $\alpha$  is taken to be  $0.5$ .

corresponding to rather "stiff" chains the turning point is  $v/a_0 l_c = 0.8$ . Bilayers would be formed for  $0.5 < v/a_0 l_c < 0.65$  and revert to vesicles again for  $v/a_0 l_c > 0.65$ . This remarkable phenomenon is purely a consequence of geometry and is not universal. Thus for very fluid chains, say  $\alpha = 0.25$ , vesicle size decreases monotonically until  $v/a_0 l_c = 0.5$ , below which value cylinders are the favoured structure.

## 5.2 NON-LINEAR EXTENSIONS

Subject to those complications just discussed which arise due to internal packing constraints, both entropy and head-group curvature tend to favour vesicles as compared with bilayers. We wish to explore how that conclusion holds within a wider framework. That is, we now admit the possibility that curvature effects are large, so that the assumption  $a = a_0$  of the zeroth-order theory would no longer be tenable. A theory which covers this situation is necessarily model dependent and non-linear, depending on unknown details of molecular interaction.

Perhaps the simplest mathematical description of head-group interactions for non-ionic surfactants is *via* the capacitor model: Imagine that  $D$  is the average distance between positive and negative charges which form a dipolar head group (*i.e.*  $qD$  is the dipole moment where  $q$  represents unit charge). Then for a bilayer we should have

$$\mu_{\infty}^s = \gamma a + \frac{2\pi q^2 D}{\epsilon a}, \quad a_0 = \sqrt{\frac{2\pi q^2 D}{\epsilon \gamma}}, \quad (19)$$

where  $\epsilon$  is the "capacitor" dielectric constant. (A similar model might be used to describe ionic surfactants with  $D$  the Debye length.) Corresponding to eqn (11), we now have for vesicles

$$\mu_{\text{ves}}^s = \frac{N_c \mu_c + N_l \mu_l}{N} \quad (20a)$$

$$\mu_c/\gamma = a_c + \frac{a_0^2}{a_c(1+D/R_c)}; \quad \mu_l/\gamma = a_l + \frac{a_0^2}{a_l(1-D/R_l)}, \quad (20b)$$

where

$$N_e = \frac{4\pi}{3v}(R_e^3 - R_m^3); \quad N_i = \frac{4\pi}{3v}(R_m^3 - R_i^3); \quad N = N_e + N_i. \quad (21)$$

Recall that  $R_e$ ,  $R_m$  and  $R_i$  are external, middle and internal radii, respectively, with  $N_e$  and  $N_i$  the number of external and internal surfactant molecules. Obviously  $R_e > R_m > R_i > D$ .

Optimisation of  $\mu_{ves}^s$  is a tedious but straightforward numerical problem. Typical results are given in table 3, which should be compared with table 2. (For definiteness we take  $q = 4.8 \times 10^{-10}$  e.s.u.,  $\epsilon = 78$ ,  $\gamma = 50$  dyn cm $^{-1}$  so that  $a_0 = \sqrt{(372D)} \text{ \AA}^2$ , where  $D$  is measured in  $\text{\AA}$ .) The particular algorithm used was that developed by Brent.<sup>20</sup>

TABLE 3.—TYPICAL VESICLE PARAMETERS IN CAPACITANCE MODEL FOR HEAD-GROUP INTERACTION WITH  $\alpha = 0.5$ ,  $v = 1063 \text{ \AA}^3$ ,  $l_c = 20 \text{ \AA}$

$D/\text{\AA}^2$	$v/a_0 l_c$	$a_0/\text{\AA}^2$	$a_e/\text{\AA}^2$	$a_i/\text{\AA}^2$	$R_e/\text{\AA}^2$	$R_i/\text{\AA}$	$l_e/\text{\AA}$	$l_i/\text{\AA}$	$N_e$	$N_i/\text{\AA}$
7.55	1	53	53	53	$\infty$	$\infty$	20	20	$\infty$	$\infty$
8	(0.97)	54.5	54.8	55.3	646	607	20	18.6	95 000	83 000
10	(0.87)	61	62	68	130	96	20	13.7	3 430	1 730
12	(0.79)	67	68	85	84	53	20	10.4	1 300	430
14	(0.74)	72	68.4	88.4	83	53	20	10	1 250	390
16	(0.69)	77	67.6	89	86	55	20	10	1 365	440
18	(0.65)	82	68.4	91	92.5	63	19.3	10	1 570	550
20	(0.62)	86	72	94	112	84.6	17	10	3 150	950
22	(0.59)	90	78	98	143	118	15	10	3 270	1 780
24	(0.56)	94	84	100	200	173	13.6	10	5 800	3 750
26	(0.54)	98	90	102	303	281	12.2	10	12 800	9 680
30	(0.50)	106	106	106	$\infty$	$\infty$	10	10	$\infty$	$\infty$

An internal packing condition  $l_i \geq \alpha l_c$  is again necessary to obtain sensible results. Variation of  $a_e$ ,  $a_i$  from  $a_0$  is considerable at larger head-group areas. Similarly, predicted vesicle sizes can vary by up to a factor of 2 from the zeroth-order theory in extreme cases. Similar results emerge for different values of  $\alpha$ . Despite these quantitative differences it does appear that non-linearity does not affect the main conclusions of the zeroth-order theory.

We have to emphasize that whatever the nature of the forces between head groups (and chains) which give rise to curvature, these may well inject non-linear effects and precise quantitative predictions are not feasible at the present time. However, the general pattern which emerges from the zeroth-order theory seems to be on fairly safe ground. Moreover while the theory strictly depends on four parameters ( $v$ ,  $a_0$ ,  $l_c$ ,  $\alpha$ ) the substantial predictions rely only on the surfactant parameter  $v/a_0 l_c$  and are independent of the detailed form of the forces. The vexed and delicate question of the stability of vesicles must remain open in general, depending as it does on chain stiffness (subsumed in the parameter  $\alpha$ ) and the competition between curvature and interaction between bilayers. The answer will differ from surfactant to surfactant and depends on temperature.

## 6. MICROEMULSIONS

## 6.1 THERMODYNAMICS OF MICROEMULSIONS

We now broaden our enquiry to include oil-water-surfactant systems. In the absence of surfactant, oil and water will separate into two phases (unless the volume fraction of oil is extremely low or very close to unity). In this case the oil aggregate is arbitrarily large, its size being determined by the *absolute* amount of oil present. When surfactant is added, some surfactant molecules will go to the oil-water interface and lower the interfacial tension. With the addition of still more surfactant, several possibilities arise. Aggregates may appear in either the water phase or the oil phase. These aggregates may be micelles containing a little oil, dispersed in water or inverted micelles containing a little water, dispersed in oil; or large drops of oil (or water) with surfactant at the interface, dispersed in water (or oil).<sup>21,22</sup> It is possible to solubilize all the oil (or water). Another possibility is the occurrence of a three phase system: water, oil and so-called surfactant phase which contains all three components.<sup>21</sup> Once aggregates form, additional surfactant will be consumed in the formation of aggregates and will have little effect on the tension of the oil-water interface. We here use the term microemulsion to mean a thermodynamically stable dispersion of large oil and surfactant or water and surfactant aggregates. We make no distinction between large swollen micelles and microemulsions. Microemulsions are often monodisperse<sup>23</sup> and the size of the drops is determined by the relative proportions of oil, water and surfactant, not by the absolute amount of oil, in the solution. These are by definition one phase systems.

The thermodynamic approach developed in the previous sections can be extended to deal with these systems. Microemulsion drops can be treated in a similar way to pure surfactant aggregates and the distribution determined by the law of mass action. As for surfactants where a simpler picture is provided by the less rigorous pseudo-phase approximation; a simpler picture of microemulsions is also obtained if we ignore translational entropy of the aggregates.

Recall that for a surfactant solution the aggregates which form (in the pseudo-phase approximation) are those with  $\min \mu_N^\circ$  and the concentration at which they form (the c.m.c.) is given by

$$\mu_N^\circ = \mu_1^\circ + kT \ln X_1 \equiv \mu.$$

This result was derived as an approximation to the law of mass action, but it can be seen more directly as follows. If some of the molecules were arranged in non-optimal aggregates they could lower their total free energy by rearranging into optimal aggregates. If  $\mu < \mu_N^\circ$  the total free energy would be lowered by dissolution of some or all of the aggregates. We note also for optimal aggregates (defined by  $\partial \mu_N / \partial N = 0$ ) that

$$\frac{\partial}{\partial N} (N \mu_N^\circ) = \mu_N^\circ$$

so that when  $\mu = \min \mu_N^\circ$  the optimal aggregates are in chemical equilibrium with the surfactant monomers.

In the case of multicomponent systems a similar argument can be invoked. The determination of which mixed aggregates form is a little more complicated. Here the composition of the aggregates will be dependent on the overall composition of the mixture. (This is abundantly clear if almost all the solute molecules are aggregated.)

If  $G_{M,N} \equiv (M+N)\mu_{M,N}^\circ$  denotes the free energy† of an aggregate containing  $M$  molecules of oil‡ and  $N$  molecules of surfactant then clearly out of all possible aggregates with the given composition  $X = N/(M+N)$  those which form must have the min  $\mu_{M,N}^\circ$ . The minimization is taken with respect to shape and size, *etc.*, at fixed composition.

The composition of aggregates will be uniform if  $g = \min \mu_{M,N}^\circ$  is a concave function of  $X$ ; i.e.  $\partial^2 g / \partial x^2 \geq 0$ . However, if  $g$  is not a concave function the solution may contain a variety of aggregates of differing composition|| (cf. fig. 3).

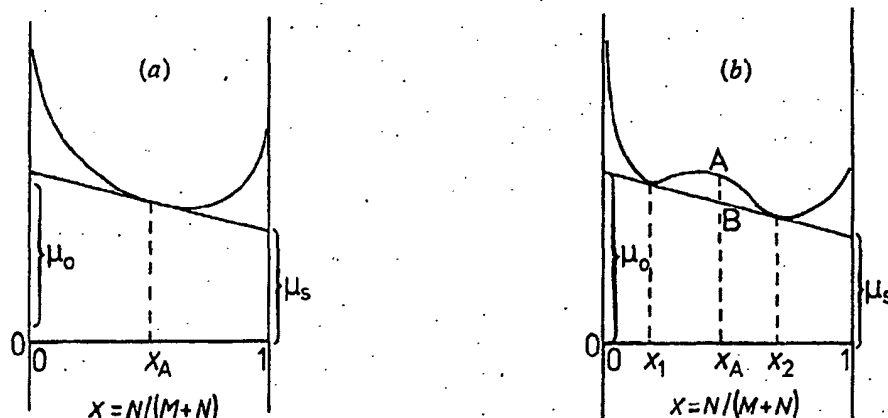


FIG. 3.—Diagram illustrating determination of aggregate composition: (a)  $g$  is everywhere a concave function of  $X$ . If chemical potential of one component is given (e.g.  $\mu_0$ ), composition  $X_A$  of aggregates and chemical potential of other component is determined. (b)  $g$  is not everywhere concave. For a particular value of  $\mu_0$  and  $\mu_s$  the tangent touches the curve at two points. In this case a mixture of aggregates of compositions  $X_1, X_2$  will occur. A system comprising aggregates of intermediate composition would have a higher free energy  $g_A$  than the mixture  $g_B$ .

If we wish to determine the composition of the aggregates given the overall composition of the solution it is necessary to determine the concentrations, or equivalently the chemical potentials, of the monomers. The general problem is difficult. The easiest way to proceed is *via* an indirect route. We assume a value for the chemical potential of one species. This allows us to determine the corresponding value of the chemical potential of the other species. The composition of the corresponding aggregate and overall composition of the corresponding solution follow. The procedure is iterated until the required overall composition is achieved. One special case, indeed one of much interest, can be handled with relative ease: For a microemulsion solution in the presence of excess oil the chemical potential of one species, oil, is in fact prescribed.

Suppose then that we are given the chemical potential  $\mu_0$  of the oil (i.e. of the monomers; and also of bulk oil when excess oil is present). We wish to show that the aggregates (and there may be more than one type) which can occur for this  $\mu_0$  are those for which the expression  $\mu_s(M, N) \equiv (G_{M,N} - M\mu_0)/N$  is a minimum. The

† It is argued in the Appendix that  $(M+N)\mu_{M,N}^\circ$  is the Helmholtz free energy  $+ P_0 V_{\text{agg}}$  where  $P_0$  is the (external) pressure of the solution.

‡ The argument holds for water instead of oil.

|| The argument here parallels the argument that the Gibbs free energy of a mixture of two components divided by the total number of molecules must be a concave function of the mole fraction  $X$ ; otherwise a double tangent construction is required to render the Gibbs free energy per molecule  $g$  concave.<sup>24</sup> An interval for which  $\partial^2 g / \partial x^2 = 0$  corresponds to phase separation.

corresponding value of the surfactant chemical potential  $\mu_s$  is equal to this minimum value; *i.e.*

$$\mu_s = \min_{M,N} \mu_s(M, N) = \min_{M,N} (G_{M,N}^\circ - M\mu_o)/N. \quad (22)$$

The proof is as follows. If  $\mu_s < \min \mu_s(M, N)$ , then  $G_{M,N}^\circ > M\mu_o + N\mu_s$  for all  $M$  and  $N$ . That is, the free energy of every aggregate exceeds the free energy of the monomers obtained by dispersing the aggregate. But if  $\mu_s > \min \mu_s(M, N)$ , then  $G_{M,N}^\circ < M\mu_o + N\mu_s$  for some  $M, N$ . The formation of aggregates with this  $M$  and  $N$  would lower the free energy. The problem is then reduced to finding  $\min \mu_s(M, N)$ .

We shall see in the following sections how curvature energy and packing determine which aggregates (normal or inverse) will form. The formation of a microemulsion depends on the competition between micellar structures which absorb little oil and large "swollen" micelles which contain a large amount of oil.

## 6.2 PACKING IN MICROEMULSION DROPS

As in the case of surfactants we require now a model of microemulsion drops which will allow us to write down an explicit expression for  $\mu_s(M, N)$ . The simplest model of an aggregate is represented in fig. 4. For the time being we admit no specific

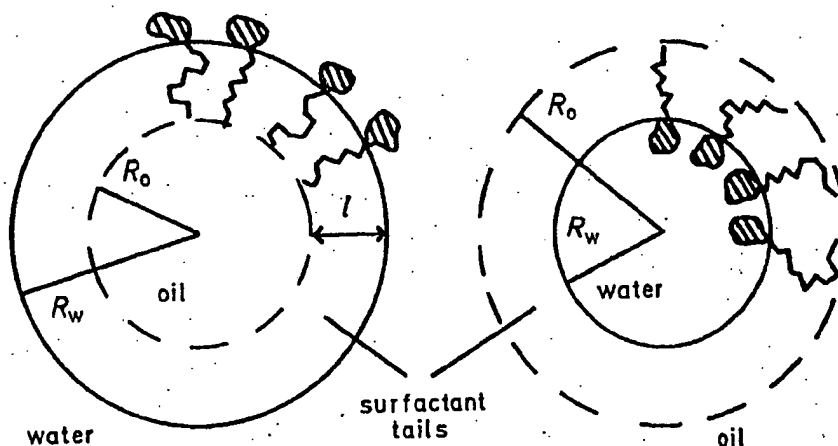


FIG. 4.—Geometry of microemulsion drops: no penetration model.

interaction between the oil and surfactant chains. The generalization of  $\mu_N^\circ$  discussed in section 2 is

$$G_{M,N}^\circ = M\mu_o(\text{bulk}) + N\{\mu_N^B + \gamma[a + a_0^2/a(1 + D/R_w)]\}, \quad (23)$$

where  $a = A/N$  is the total area of the drop divided by the number of surfactant molecules, and  $\mu_o(\text{bulk})$  is the chemical potential of oil (at the external pressure of the solution). It follows that the quantity to be minimized is

$$\mu_s(M, N) = \frac{M}{N}[\mu_o(\text{bulk}) - \mu_o] + \mu_N^B + \gamma[a + a_0^2/a(1 + D/R_w)], \quad (24)$$

where  $\mu_o$  is the chemical potential of the oil monomers. We restrict the argument to the case of excess oil for which  $\mu_o(\text{bulk}) = \mu_o$ . We emphasize again that the particular form of curvature energy is immaterial for the argument which follows.

The variables  $a$  and  $R$  are specified through the relations

$$V = Mv_{oil} + Nv = \frac{4\pi}{3}R_w^3, \quad a = \frac{4\pi R_w^2}{N} \quad (25)$$

so that the minimum  $\mu_s(M, N)$  can be obtained by minimizing with respect to  $R_w$  and  $a$  in succession subject to the packing constraint  $l \leq l_c$ . The minimum at fixed  $a$  is given by the smallest value of  $R_w$  allowed by packing. This corresponds to a drop with  $l = l_c$  and no interpenetration of oil and surfactant for  $v/a_0l_c > \frac{1}{3}$  or a spherical micelle for  $v/a_0l_c < \frac{1}{3}$ . For water in oil microemulsions a similar argument leads to a form for  $\mu_s(M, N)$  identical to eqn (24) but with  $\mu_o$  replaced by  $\mu_w$  and  $D$  replaced by  $-D$ . In this case the minimum corresponds to the largest  $R_w$  allowed by packing,  $l = l_c$ , and again no interpenetration.

If curvature is assumed to be small, we can take  $a = a_0$  and consider optimal drop parameters as a function of  $v/a_0l_c$ . We have

$$\frac{4\pi}{3}|R_o^3 - R_w^3| = Nv; \quad |R_o - R_w| = l_c, \quad 4\pi R_w^2 = Na_0, \quad (26)$$

whence

$$\frac{3v}{a_0l_c} = \frac{R_o^2 + R_oR_w + R_w^2}{3R_w^2} \equiv 1 + x + x^2, \quad x = \frac{R_o}{R_w} \quad (27)$$

with solution

$$x = \sqrt{\frac{3v}{a_0l_c} - \frac{3}{4}} - \frac{1}{2}. \quad (28)$$

Thus  $v/a_0l_c$  determines  $x$  and hence  $R_o$  and  $R_w$  are determined if  $l_c$  is known separately. Since  $R_o/R_w < 1$ , for normal drops  $v/a_0l_c < 1$ . The volume fraction of oil within the drop is

$$\phi_{oil} \equiv \frac{V_{oil}}{V_{oil} + V_{surf}} = x^3. \quad (29)$$

For inverted drops the same equations hold, but now  $R_o - R_w = l_c$  and the condition for existence is  $v/a_0l_c > 1$ . For inverted drops

$$\phi_{water} \equiv \frac{V_{water}}{V_{water} + V_{surf}} = \frac{1}{x^3}. \quad (30)$$

Volume fractions and other parameters of microemulsion drops are tabulated in table 4. Note that for oil-in-water systems geometry dictates that microemulsions, as opposed to swollen micelles, begin at  $v/a_0l_c \geq 0.8$  (in the sense that  $\phi_{oil} > \frac{1}{2}$ ). The problem of encapsulating a substantial oil fraction is critically sensitive to  $v/a_0l_c$ .

The observation that for inverted drops the aggregate of minimum free energy corresponds to the *largest*  $R_w$  allowed by packing has an interesting consequence for concentrated dispersions. For a given surfactant which forms inverse structures ( $v/a_0l_c > 1$ ), uptake of water is greater on addition of oil. This can be illustrated by the simple model calculation for inverted micelles discussed below. Column 5 of table 4 lists maximum uptake of water by inverse micellar solutions as calculated from this model. These results are obtained as follows. Consider an inverse micellar system to be a dispersion of equal-sized spheres of water in surfactant such that the head groups of all surfactant molecules reside at a water interface. For simplicity



TABLE 4.—(a) OPTIMAL PARAMETERS OF OIL-IN-WATER MICROEMULSIONS ASSUMING  $a = a_0$ , NO PENETRATION OF OIL INTO TAIL REGION

$v/a_0 l_c$	$x = R_o/R_w$	$R_w/l_c$	$\phi_{oil}$
0.5	0.36	1.58	0.05
0.6	0.52	2.10	0.14
0.7	0.66	2.96	0.29
0.8	0.78	4.64	0.48
0.85	0.84	6.31	0.60
0.9	0.89	9.65	0.72
0.95	0.95	19.70	0.86
1	1	$\infty$	1

$R_o/l_c = R_w/l_c - 1$

TABLE 4.—(b) OPTIMAL PARAMETERS OF WATER-IN-OIL MICROEMULSIONS ( $a = a_0$ , NO PENETRATION)

$v/a_0 l_c$	$x = R_o/R_w$	$R_w/l_c$	$\phi_{water}$	$\phi_w$ (inverted micelles)
1	1	$\infty$	1	0.40
1.1	1.10	10.32	0.76	0.34
1.2	1.19	5.31	0.60	0.29
1.3	1.27	3.64	0.48	0.26
1.4	1.36	2.80	0.40	0.22
1.5	1.36	2.80	0.40	0.20
1.6	1.51	1.95	0.29	0.18
1.8	1.59	1.71	0.25	0.14
2.0	1.79	1.26	0.57	0.12

$R_o/l_c = R_w/l_c - 1$

ignore head-group size. The volume fraction of water  $\phi_w$  and radius  $R_w$  of the water spheres is easily shown to be  $\phi_w = R_w/(3v/a_0 + R_w)$ . Let  $d_{max}$  be the maximum distance of any point of the surfactant region from the centre of the nearest water sphere. Clearly  $d_{max} \leq R_w + l_c$ . For a given volume fraction  $\phi_w$ , the minimum value of  $d_{max}$  obtains for a f.c.c. lattice and can be shown to be

$$\sqrt{\frac{3}{2}} \left( \frac{\pi \sqrt{2}}{6 \phi_w} \right)^{1/3} R_w.$$

Hence the largest volume fraction allowed is that corresponding to a f.c.c. lattice with  $d_{max} + R_w + l_c$ . Eliminating  $R_w$ , the tabulated results follow.

### 6.3 EFFECT OF CURVATURE IN MICROEMULSION FORMATION (H.L.B.)

If  $v$ ,  $a_0$  and  $l_c$  can be estimated, table 4 gives some idea of the size of drops expected and therefore of design characteristics. The model is clearly deficient in at least two important respects. One is its lack of oil specificity which problem we defer. The other is the effect of curvature which can affect allowed optimal structures in some circumstances. A mathematical description of curvature effects which spans

the full gamut of expectations and trends at a qualitative level only can be formulated as follows:

(1) For non-ionic surfactants we have for the surface contribution to  $\mu_s(M, N)$

$$\mu_N^s = \gamma \left( a + \frac{a_0^2}{a(1+D/R)} \right), \quad (31)$$

where, as for eqn (18)–(20) the bilayer optimal area can be characterized for convenience in terms of a capacitor model for head group interactions,  $a_0 = \sqrt{(2\pi q^2 D / \epsilon \gamma)}$ . As for our analysis of vesicles, for definiteness only we take  $a_0 = \sqrt{(372 D / \text{\AA}^2)}$ .

(2) An identical description can be used for ionic surfactants. Debye–Hückel theory leads again to the capacitor model with  $D = \kappa^{-1}$ , the Debye length, with

$$\kappa^2 = \frac{8\pi q^2}{\epsilon kT} n_0$$

for a 1:1 electrolyte.  $n_0$  is the bulk electrolyte concentration. Taking  $\epsilon = 78$  for water,  $q = 4.8 \times 10^{-10}$  e.s.u.,  $kT = 4.116 \times 10^{-14}$  erg at 25°C, we have  $D = 3.03c^{-1/2}$ , where  $c$  is the salt concentration in  $\text{mol dm}^{-3}$ . Taking further  $\gamma = 50 \text{ dyn cm}^{-1}$  as the surface tension of the hydrocarbon–water interface for rough estimates we have the correlation between salt concentration and head-group area indicated in table 5. The import of table 5 is that for ionic surfactants, salt concentration or composition must provide a substantial contribution to head-group curvature and can markedly affect conditions under which microemulsions can form.

TABLE 5.—EFFECT OF SALT CONCENTRATION ON BILAYER HEAD-GROUP AREA

$c/\text{mol dm}^{-3}$	$D/\text{\AA}$	$a_0/\text{\AA}^2$	$v/a_0 l_c (v/l_c = 30 \text{\AA}^2)$
1	3.03	33	0.893
0.5	4.29	40	0.751
0.1	10.0	60	0.502
0.05	13.6	71	0.422
0.01	30.3	106	0.282
0.001	96	189	0.159

Clearly both models of curvature encompassed in eqn (27) are extreme and are not to be taken at a quantitative level. However, characterization of curvature through such models may be useful in two respects: (a) Assignment of  $D$  to a particular non-ionic surfactant/water system can be used to predict behaviour for others in a homologous series (e.g.  $C_n\text{EO}_m$ ); similarly for ionic surfactants with varying salt concentrations; (b) The very extremity of such models is useful if, given such flexibility, the substantial conclusions of the zeroth-order theory are confirmed.

We consider then the form eqn (31) and optimize  $\mu_N^s$  with respect to  $a$ , taking  $R = 3v/a$  for spherical micelles and  $R_w = R = l_c / [\frac{1}{2} - \sqrt{(3v/al_c - \frac{3}{4})}]$  [eqn (28)] for microemulsion drops. Differentiating eqn (31) we have

$$\frac{1}{\gamma} \frac{\partial \mu_N^s}{\partial a} = 1 - \frac{a_0^2}{a^2} \frac{R}{(R+D)^2} \left( R + D - D \frac{a}{R} \frac{\partial R}{\partial a} \right), \quad (32)$$

where

$$\frac{a}{R} \frac{\partial R}{\partial a} = -1 \quad \text{spherical micelles } (R = 3v/a) \quad (33a)$$

$$\frac{a}{R} \frac{\partial R}{\partial a} = -\frac{3}{2} \frac{(v/al_c)(R/l_c)}{(\frac{3}{2} - l_c/R)} \quad \text{spherical drops.} \quad (33b)$$

For  $v/al_c > \frac{1}{3}$  we have drops and for  $v/al_c < \frac{1}{3}$  micelles. At  $v/al_c = \frac{1}{3}$ ,  $R = l_c$ , eqn (33b) reduces to

$$\frac{a}{R} \frac{\partial R}{\partial a} = -1$$

so that  $\partial \mu_N^S / \partial a$  is continuous. Thus we can find the optimum structure if it exists by finding the zero of  $\partial \mu_N^S / \partial a$ . The same equations hold for inverted drops if  $R$  is replaced by  $-R$ . The equations have been solved numerically for a range of surfactant parameters. Typical results are displayed in table 6.

TABLE 6.—EFFECTS OF HEAD-GROUP CURVATURE ON PARAMETERS OF MICROEMULSION DROPS

(i)  $l_c = 17.5 \text{ \AA}$ ,  $v = 1060 \text{ \AA}^3$  (TYPICAL DOUBLE-CHAINED SURFACTANT)

$D/\text{\AA}$	$a_0/\text{\AA}^2$	$a/\text{\AA}^2$	$R_w/\text{\AA}$	$R_w^0/\text{\AA}$	$v/a_0 l_c$	$v/al_c$
1	19.3	21	-13.5	-13	3.1	2.9
3	33.4	38.5	-36.5	-27	1.8	1.56
5	43	51	-102	-50	1.4	1.2
7	51	60	+3663	-105	1.18	0.96
9	58	68	144	-479	1.04	0.86
11	64	74	85	276	0.94	0.81
13	69.5	79.5	65	121	0.86	0.75
17	80	89	47	62	0.74	0.67
21	88	94	42	48	0.68	0.64
30	106	104	34.5	33	0.57	0.57
43	126	112	30.5	26	0.47	0.54
96	189	124	26	16	0.32	0.48
303	336	132	24	9	0.18	0.45

(ii)  $l_c = 17.5 \text{ \AA}$ ,  $v = 525 \text{ \AA}^3$  (TYPICAL SINGLE-CHAIN SURFACTANT)

$D/\text{\AA}$	$a_0/\text{\AA}^2$	$a/\text{\AA}^2$	$R_w/\text{\AA}$	$R_w^0/\text{\AA}$	$v/a_0 l_c$	$v/al_c$
3	33	35	107	165	0.90	0.84
9	56	58	28.5	29	0.52	0.51
13	69.5	67	24	23	0.43	0.45
17	81	73	21	19	0.37	0.41
21	88	77	20.5	18	0.34	0.39
30	105	84	19	15	0.28	0.36
43	126	89	18	12	0.24	0.34
76	189	97	16	8	0.16	0.30
303	336	103	15	4.7	0.09	0.29

Comparison of microemulsion drop parameters as given by zeroth-order theory ( $a = a_0$ ) with predictions of capacitor model for head-group curvature. Negative radii correspond to inverted drops.  $R_w^0$  denotes  $R_w$  as computed by zeroth-order theory.

Several remarks are in order. Recall that if curvature is ignored, the zeroth-order approximation predicts (i) micelles  $v/a_0l_c < \frac{1}{3}$ ; (ii) normal drops  $\frac{1}{3} < v/a_0l_c < 1$ ; (iii) inverted drops  $v/a_0l_c > 1$ . By comparison, when curvature is taken into account, the situation is modified. Now we predict normal drops in a region where formerly we would have expected inverted drops. For smaller values of  $v/a_0l_c$  curvature effects give larger drops, indeed can lead to drops where zeroth-order theory gives micelles. Note that for single-chained surfactants inverted drops only occur for low values of  $a_0$ , i.e. very weak head-group interactions. The indications are that curvature plays a larger role in the determination of the dimensions of microemulsion drops than for vesicles, where there is a partial cancellation of curvature effects.

It can easily be shown from eqn (32)–(33) that the condition for existence of inverted drops is

$$v/a_0l_c > \sqrt{(1 + D/l_c)},$$

and for micelles

$$v/a_0l_c < \frac{1}{3} \frac{\sqrt{(1 + 2D/l_c)}}{(1 + D/l_c)}.$$

Note that the zeroth-order theory is in rough qualitative agreement. In essence then, these calculations quantify the older notion of hydrophilic–lipophilic balance (h.l.b.). We shall expand on this in the following section.

## 7. DISCUSSION AND CONCLUSION

### 7.1 RECAPITULATION

We are now in a position to put the whole story together. To recapitulate: We have presented a simple model of surfactant aggregation in which the aggregate size, shape and composition is determined essentially from the packing ratio  $v/a_0l_c$ . Components of this apparently magic number are  $v$ , the partial molecular volume of surfactant,  $a_0$ , the head-group area of a surfactant molecule and  $l_c$ , which is the maximum chain length. The head-group area  $a_0$  is assumed to be determined by the competition between head-group interactions and the interfacial tension between the hydrocarbon tails and water. It is thus primarily a property of the head group. The more “hydrophilic” the head group the larger  $a_0$  will be. The parameter  $l_c$  is assumed to be a property primarily of the tail. It is taken to be the maximum length of the tail in the sense that a further increase in its length will result in a large increase in free energy.

We have generally assumed that the tails are completely flexible and liquid-like provided their length  $l$  is less than  $l_c$ , and that  $l$  is constrained to be less than  $l_c$ . The aggregate then is assumed to adopt the optimum head-group area. Then the head-group curvature energy, which is treated as a perturbation, is assumed to shrink the aggregate to the smallest aggregate satisfying the above constraints. The smallest aggregate, for  $v/a_0l_c > \frac{1}{3}$ , will have  $l = l_c$ . However, the situation would not change significantly (except for vesicles) if  $l_c$  represented an optimum length rather than a maximum length. It is essentially the tail length at which the tail free energy resists further lengthening under the influence of head-group curvature energy.

In the case of vesicles we have found it necessary to introduce a lower limit  $\alpha l_c$  on the tail length. The free energy of the tails is assumed to rise rapidly if  $l$  falls below  $\alpha l_c$ . However, it would appear that tail lengths can vary by at least a factor of two.<sup>19</sup>

The main omission in this lowest level theory is the possible effect of curvature on the free energy of both head group and tail. We have explored this matter in sections 4.2, 5.2 and 6.2.

## 7.2 H.L.B., AND EFFECTS OF SALT, TEMPERATURE, AND COSURFACTANTS

The packing ratio  $v/a_0l_c$  provides a measure of the hydrophilic-lipophilic balance (h.l.b.). For values of  $v/a_0l_c < 1$  we predict "normal", *i.e.* convex, aggregates and for  $v/a_0l_c > 1$  we predict inverse micelles and drops. That is, for  $v/a_0l_c < 1$  we predict a tendency to curve spontaneously into normal structures and for  $v/a_0l_c > 1$  to curve spontaneously into inverse structures.

The packing ratio is affected by many factors including hydrophilicity of head group, ionic strength of solution, pH, temperature and the addition of lipophilic compounds such as cosurfactants. The more hydrophilic the head group the stronger the repulsion between the head group and the larger  $a_0$  will be. The smaller the value for  $v/a_0l_c$ , the smaller will be the micelles formed. Thus (single chained) ionic surfactants (at low salt concentrations) tend to form small spherical or globular micelles<sup>1</sup> whereas monoglycerides tend not to form micelles at all but form vesicles or liposomes or lamellar particles in dilute solution.<sup>12,16</sup> The non-ionic surfactants polyoxyethylene dodecyl ether ( $C_{12}E_m$ ) form micelles at room temperature if their head groups are long enough (*e.g.*  $C_{12}E_6$ ,  $C_{12}E_8$ ) but  $C_{12}E_4$  forms lamellar dispersions.<sup>12</sup>

The addition of NaCl to micellar solutions of sodium dodecylsulphate causes the micelles to grow in size and become long rod-shaped micelles.<sup>1,28</sup> Similarly the addition of HCl to micellar solutions of potassium oleate causes the micelles to grow, and, if the pH is lowered sufficiently, the solution goes cloudy and contains liposomes.<sup>25</sup> In both cases the repulsion between head groups decreases, *i.e.*  $a_0$  decreases and  $v/a_0l_c$  increases, so that our theory would predict a change from spherical micelles to cylindrical micelles and eventually to vesicles.

The incorporation of cosurfactants into surfactant aggregates would be expected to increase the mean volume per surfactant molecule without affecting appreciably either  $a_0$  or  $l_c$ .<sup>26</sup> Consequently  $v/a_0l_c$  would increase with addition of cosurfactant, leading successively to an increase in micelle size, the formation of long rod-shaped micelles and eventually the formation of lamellar phase or lamellar dispersion.<sup>26,27</sup> The theory also predicts the observed increase in stabilization of hydrocarbons by ionic surfactant solutions due to the addition of cosurfactants (*e.g.* *cf.* Shinoda<sup>22</sup>). There is no need to invoke specific interactions (which are discounted by Shinoda and Friberg,<sup>21</sup> and by Wennerström and Lindman<sup>26,28</sup>).

The effect of temperature on  $v/a_0l_c$  is difficult to predict without a better understanding of the forces at play. However, many of the observed phenomena for biological lipids<sup>2,12,21</sup> as well as<sup>12,21</sup> for non-ionic surfactants such as poly(oxyethylene) alkyl ethers may be accounted for if we assume  $v/a_0l_c$  increases with temperature. Micellar size would be expected to increase with temperature. Non-ionic surfactants do tend to go cloudy when the temperature is raised above the aptly named cloudy point<sup>22</sup> indicating the formation of large aggregates [or flocculation of aggregates, the phase diagrams of poly(oxyethylene) alkyl ethers display a lower consolute curve<sup>22</sup> near the cloud point which indicates an attractive interaction between the aggregates above the critical point]. The surfactant  $C_{12}E_4$  forms<sup>12</sup> a lamellar dispersion at still higher temperatures.

If  $v/a_0l_c$  increases with temperature one would expect the solubilisation of hydrocarbons in non-ionic surfactants to increase with temperature (as observed)<sup>22</sup> until  $v/a_0l_c$  reached the value 1 where phase inversion would be expected. At higher temperatures water-in-oil microemulsions would be expected and the solubilisation of water would decrease as temperature rises (again as observed).<sup>21,22</sup>

As  $a_0$  increases with increase in length of the poly(oxyethylene) head group we would expect then an increase in the cloud point and phase-inversion temperature (p.i.t.) with head-group length (as observed).<sup>22</sup>

### 7.3 OIL SPECIFICITY

The model of microemulsion drops presented in section 6 ignored the possibility that the oil might penetrate into the surfactant interphase. Some phenomena of oil solubilisation appear to require the assumption that hydrocarbons, some more than others, do penetrate into the interphase. As a consequence, the packing ratio  $v/a_0l_c$  is effectively increased, due to an increase in the interphase volume per surfactant molecule.

Experiments on the solubility of hydrocarbons in lipid lamellar phases<sup>29,30</sup> suggest that smaller alkanes penetrate into the surfactant layers more than larger alkanes. If we assume this to be true then this accounts for the variation with alkane chain length of cloud points of non-ionic surfactant solutions with saturated hydrocarbon.<sup>22</sup> This observation can be illustrated and quantified through the following example. From the experiments discussed by Gruen and Haydon<sup>29</sup> we see that decane swells the hydrocarbon layer of a glycerol monooleate black film to double its thickness (from 24 to 48 Å). Experimentally it is known that the head-group area remains constant. Thus the volume per surfactant molecule doubles and so  $v/a_0l_c$  also doubles. On the other hand, the p.i.t. (which corresponds to  $v/a_0l_c = 1$ ) of the decane- $C_{12}E_4$ -water system<sup>31</sup> is approximately 20°C which is coincidentally the onset temperature of lamellar dispersion for aqueous solutions of  $C_{12}E_4$ <sup>12</sup> corresponding to  $v/a_0l_c = \frac{1}{2}$ . Thus also in this example decane appears to swell the surfactant hydrocarbon tail volume by a factor of two. With longer chain hydrocarbons  $v/a_0l_c$  changes less markedly<sup>29,30</sup> (e.g. for hexadecane by a factor of  $\frac{4}{3}$ ).

Long-chain alkanes elevate the cloud point.<sup>22</sup> This is to be expected since  $v/a_0l_c$  is hardly altered, and our model predicts that large, non-spherical micelles will be replaced by small microemulsion drops.

### 7.4 THE INTERFACIAL TENSION CONTROVERSY AND THE SURFACTANT PHASE

Some authors<sup>32</sup> have suggested that a microemulsion forms spontaneously as a result of the interfacial tension between the oil and water phases becoming zero or even taking negative values. If, on addition of surfactant or cosurfactant to the system, the interfacial tension becomes negative the system would tend to increase the area of the oil-water interface, taking up surfactant from the solution, until the interfacial tension returned to zero. The system would then be stable because: If the area were to decrease, the interfacial tension would become negative, favouring an increase in the area, whereas if the area were to increase the interfacial tension would become positive favouring a decrease in area. However, if we ignore such factors as curvature energy, the system would be indifferent to whether an oil-in-water or water-in-oil emulsion formed, or to what size distribution of drops formed, provided only that the total area achieved the required value.

By contrast, if we invoke a curvature energy to determine the size of the drops and to determine which phase is dispersed in the other, we find that the microemulsion will form while the tension of the oil-water interface is still slightly positive.

This can be seen from the following argument: If curvature energy favours a drop of finite size, it will do so only because this drop has the minimum value of  $(G_{M,N} - M\mu_O)/N$  or of  $(G_{M,N} - M\mu_W)/N$ . The drops will form when the chemical potential of the surfactant is equal to this minimum value. On the other hand, for an infinite drop of oil  $(G_{M,N} - M\mu_O)/N$  represents the interfacial Gibbs free energy per surfactant molecule and if the interfacial tension of the infinite drop is zero, this interfacial Gibbs free energy is also equal to the chemical potential of the surfactant. Thus the finite drop will form at a surfactant chemical potential lower than the chemical potential at zero interfacial tension, *i.e.* when the interfacial tension is positive.

Shinoda and Friberg<sup>21</sup> sketch the variation of interfacial tension between the oil and water phases with temperature for a system containing equal amounts of water and oil [47.5 wt %, and 5 wt % of poly(oxyethylene)nonylphenyl ether]. The interfacial tension drops to a very low value at the p.i.t. This might be understood roughly from our model if we assume again that  $v/a_0l_c$  increases with temperature, taking on the value unity at the p.i.t. Below the p.i.t.  $v/a_0l_c < 1$ , curvature energy favours an oil water dispersion and this implies a slightly positive interfacial tension. At the p.i.t.  $v/a_0l_c = 1$ , curvature energy favours zero curvature leading to a zero interfacial tension. At and near the p.i.t. therefore one expects either large drops with little curvature or an essentially lamellar structure, or some such bicontinuous phase.<sup>37,38</sup> Such large structures would be expected to interact strongly and form a separate phase; hence the surfactant phase which is commonly observed<sup>21</sup> at the p.i.t. The above argument and the experimental data suggest then that not only can microemulsions form at positive interfacial tension, but that a positive tension is in fact required. Very small interfacial tensions will occur only when the surfactant phase forms.

## 7.5 INTERACTIONS

So far we have not taken interactions between aggregates into account. The theory has been restricted to dilute oil-in-water dispersions in the presence of excess oil, or *vice versa*. We have correlated the type of microemulsion which forms to the type of aggregate which forms in the absence of oil. If we ignore the penetration of oil into the surfactant tails we would predict that surfactants forming normal micelles or vesicles should, on addition of oil, form small swollen micelles or microemulsion drops; and that surfactants which form inverse micelles should form water-in-oil dispersions on the addition of oil. The type of aggregates formed by surfactant solutions can change from normal to inverse structures on increase in temperature or addition of cosurfactant. Penetration of oil into the surfactant tails will shift the balance towards inverse structures.

Changing the water content of a surfactant solution can also change the type of structure which is observed.<sup>12,27</sup> There are a number of possible related reasons for this. Firstly, for a fixed volume fraction the distance between aggregates can be increased by decreasing the area per head group which, through the packing conditions, can change the shape from sphere to cylinder or from cylinder to lamellar. Increasing the distance between aggregates may decrease the (repulsive hydration or ionic) interaction energy.<sup>33</sup> Secondly, the distance between aggregates can be increased by changing the shape from spherical to cylindrical or from cylindrical to lamellar, thus decreasing the interaction energy at the expense of

curvature energy. Thirdly, decrease in water content may reduce the amount of water available for hydration of the head groups. This would lead to a smaller head-group area, larger value of  $v/a_0l_c$  and thereby could possibly induce a change in shape of the structures present. Whatever the reasons, change in structure is observed in surfactant solutions with change in the concentration. One might reasonably expect that analogously to the dilute solutions considered in this paper, the type of microemulsion formed on the addition of oil might be correlated with the structures present in the absence of oil, taking into account the effects of penetration of oil into the surfactant tails. Since surfactant solutions can change from normal micellar solutions to lamellar phase to inverse micellar solutions, on decreasing the water content, one might reasonably expect that water-oil-surfactant-cosurfactant systems may change from oil-water microemulsions to water-oil microemulsions *via* a lamellar phase as is indeed commonly observed.<sup>34</sup> Some surfactant solutions form reversed hexagonal phases<sup>27</sup> so that it is not surprising to find reverse hexagonal phases in oil-water-surfactant-cosurfactant systems.<sup>34</sup>

We are well aware of controversies and debate on opposing points of view. Although the older mixed-film theory has merit and embraces part of the story, Friberg and Buraczenska<sup>34</sup> have demonstrated that the distinction between microemulsions and swollen micelles is artificial. Our object in this paper has been to develop a unified approach to the subject of microemulsions which also embraces micellar systems. On that unremarkable note we rest our case.

We owe a debt to several people: The problem was posed to us by J. Th. G. Overbeek. Extensive discussions with G. J. T. Tiddy, our colleagues J. N. Israelachvili, S. Marčelja and B. A. Pailthorpe are gratefully acknowledged. We are also much indebted to S. Friberg and K. Shinoda not just for the care and thoroughness of their experiments, but also because of the clarity of their expositions on the subject. B.W.N. is grateful to S. Friberg for much encouragement.

## APPENDIX

### THE LAW OF MASS ACTION AND THE CONCEPT OF AN AGGREGATE

As already emphasized in section 2, the whole subject of association colloids is based on intuitive notions and is fraught with difficulties which devolve on definitions. The treatment in this paper is largely centred around the law of mass action and relies heavily on the notion of an aggregate (micelle, vesicle, drop, *etc.*). Here we wish to explore the difficulties and limitations involved in these concepts and the nature of the approximations made.

The concept of an aggregate is not precisely defined. There is a certain arbitrariness about any mathematically precise definition but any definition adopted must conform closely with our intuitive concepts and the predictions of the theory must not depend critically on our (arbitrary) choice of definition.

(1) A ONE-DIMENSIONAL ILLUSTRATION. The difficulties alluded to are perhaps most clearly illustrated by means of a simple one-dimensional model which allows analytic solution. Consider a one-dimensional gas with nearest-neighbour interactions. Its solution<sup>35</sup> is

$$\exp(-\beta\mu) = \int_0^\infty \exp[-\beta u(x)] \exp(-\beta px) dx, \quad (A1)$$



where  $\mu$  is the chemical potential,  $\beta = 1/kT$ ,  $p$  is the pressure and  $u(x)$  is the potential of interaction between nearest neighbours. [We assume that the distance  $x$  is normalized by some suitable length such as the diameter of molecules so that the integral in eqn (A1) is dimensionless. The pressure  $p$  is then also scaled appropriately.] Suppose that

$$u(x) = 0 \quad \text{for } x > R \quad \text{and} \quad \frac{1}{R} \int_0^R \exp[-\beta u(x)] dx \gg 1. \quad (\text{A2})$$

Then for  $\beta p R \ll 1$ , eqn (A1) can be approximated by

$$\exp(-\beta\mu) \approx \int_0^R \exp[-\beta u(x)] dx + \frac{1}{\beta p}, \quad (\text{A3})$$

whence

$$\beta p = \frac{\exp(\beta\mu)}{1 - I \exp(\beta\mu)} = \sum_{N=1}^{\infty} I^{N-1} \exp(\beta N\mu) \quad (\text{A4})$$

where

$$I = \int_0^R \exp[-\beta u(x)] dx. \quad (\text{A5})$$

Thus the concentration  $\rho$  given through the thermodynamic relation  $\rho = \partial p / \partial \mu$  is

$$\rho = \sum_{N=1}^{\infty} N I^{N-1} \exp(\beta N\mu). \quad (\text{A6})$$

By comparison the law of mass action, eqn (1), gives

$$\rho = \sum_{N=1}^{\infty} X_N = \sum_{N=1}^{\infty} N \exp(\beta N\mu) \exp(-\beta N\mu_N^0). \quad (\text{A7})$$

Eqn (A1) and (A7) are equivalent if we make the identification

$$\exp(-\beta\mu_N^0) = I^{N-1} = \int_0^R dx_1 \int_0^R dx_2 \dots \int_0^R dx_{N-1} \exp\left[-\beta \sum_{j=1}^N u(x_j)\right]. \quad (\text{A8})$$

We have shown then that, under the conditions

$$\beta p R \ll 1, \quad \frac{1}{R} \int_0^R \exp[-\beta u(x)] dx \gg 1, \quad (\text{A9})$$

the exact thermodynamic equation (A1) reduces approximately to the law of mass action with  $\mu_N^0$  determined by eqn (A8). In eqn (A8)  $\exp(-\beta\mu_N^0)$  is seen to be the partition function of an  $N$ -particle system forming an aggregate where the particles are constrained so that no two nearest neighbours are more than a distance  $R$  apart. The value of  $R$  is arbitrary so long as it satisfies condition (A2), but the conclusion is insensitive to the choice of  $R$ . The condition for the above concept of aggregate to be meaningful is that the conditions (A2) and (A8) should hold for some  $R$ , so that the potential  $u(x)$  should be strongly attractive and short-ranged.

(2) **THREE-DIMENSIONAL, ONE-COMPONENT.** For a three-dimensional system the justification of the law of mass action is rather more complicated. Consider first a

one-component system, *i.e.* ignore any solvent. The thermodynamic potential  $\Omega = -PV$  is related to the grand partition function by

$$\exp(\beta PV) = \Xi(\mu, V) = \sum_{N=0}^{\infty} \exp(\beta \mu N) Z_N(V), \quad (\text{A10})$$

where  $Z_N(V)$  is the canonical partition function which is defined by

$$Z(V) = \frac{(\lambda)^{-3N}}{N!} \int_V dr_1 \dots \int dr_N \exp[-\beta u(r_1, \dots, r_N)] \quad (\text{A11})$$

where  $\lambda = (2\pi\hbar^2/mkT)^{1/2}$  is the thermal wavelength,  $r_1, r_2, \dots, r_N$  are the coordinates of the  $N$  particles and the Hamiltonian is taken to be

$$H_N = \sum_{i=1}^N P_i^2/2m + U_N(r_1, r_2, \dots, r_N). \quad (\text{A12})$$

Assume now that some arbitrary criterion has been chosen for defining an aggregate. For example we might agree that  $m$  molecules form an aggregate of aggregation number  $m$  (an  $m$ -mer) provided that no molecule of the aggregate is more than some prescribed distance  $R$  from some other molecule of the aggregate and no subgroup of molecules is further than  $R$  from the rest of the aggregate, and provided of course that the  $m$  molecules do not belong to a larger aggregate. Then for each configuration  $(r_1, r_2, \dots, r_N)$  the  $N$  molecules partition into aggregates. Let  $n_m$  denote the number of  $m$ -mers for  $m = 1, 2, 3, \dots, N$ . The partition function  $Z_N(V)$  can then be rewritten as a sum over all configurations consistent with the partition, or

$$Z_N = \frac{1}{N! \lambda^{3N}} \sum_{\{n_m\}} \frac{N!}{\prod n_m! [(m!)^{n_m}]} \int_{\mathcal{R}(\{n_m\})} d^{3N}r \exp[-\beta u_N(r_1, \dots, r_N)], \quad (\text{A13})$$

where  $\mathcal{R}(\{n_m\})$  denotes the region of configuration space consistent with the partition into  $n_1$  monomers,  $n_2$  dimers,  $\dots$ ,  $n_m$   $m$ -mers, *etc.* We have included in eqn (A13) a combinatorial factor which gives the number of ways of partitioning  $N$  indistinguishable molecules into  $n_m$  aggregates of size  $m$ ,  $m = 1, 2, \dots, N$ . Any two configurations which differ only by the interchange of two molecules should be considered identical. The necessary approximations consist now in ignoring interactions between aggregates and extending the range of integration in eqn (A12) to allow aggregates to move through each other. The errors induced by these approximations is negligible, and allows a desirable simplification. Thus we have

$$Z_N(V) \approx \frac{1}{\lambda^{3N}} \sum_{\{n_m\}} \prod_m \frac{1}{n_m!} \left\{ \frac{V}{m!} \int dr_1, \dots, dr_{m-1} \exp\{-\beta u_m(r_1, \dots, r_m)\} \right\}^{n_m} \quad (\text{A14})$$

or

$$Z_N(V) = \frac{1}{\lambda^{3N}} \sum_{\{n_m\}} \prod_m \left( \frac{VI_m}{m!} \right)^{n_m} \quad (\text{A15})$$

where

$$I_m = \int_{\mathcal{R}_m} dr_1 \dots dr_{m-1} \exp[-\beta u_m(r_1, \dots, r_m)] \quad (\text{A16})$$

the integration being over all configurations satisfying the constraints imposed by the definition of an aggregate. If we recall that the set  $n_m$  are subject to the constraint  $\sum_m m n_m = N$ , we have from eqn (A10)

$$\begin{aligned}\Xi(\mu, V) &= \prod_m \sum_{n_m=0}^{\infty} \frac{V^{n_m}}{n_m!} \left( \frac{\exp(\beta m \mu)}{\lambda^{3m}} \right)^{n_m} \frac{I_m^{n_m}}{(m!)^{n_m}} \\ &= \exp \left( \sum_m \frac{V \exp(\beta m \mu) I_m}{\lambda^{3m} m!} \right) \equiv \exp(\beta p V).\end{aligned}\quad (\text{A17})$$

Thus

$$\rho \lambda^3 = \sum_m m \exp(\beta m \mu) \left( \frac{I_m}{m! \lambda^{3m-3}} \right). \quad (\text{A18})$$

This is equivalent to the law of mass action provided we take

$$\exp(-\beta m \mu_m^\circ) = \frac{I_m}{m! \lambda^{3m-3}}. \quad (\text{A19})$$

For the above result to have any validity it is necessary not only that the system be sufficiently dilute that interactions between aggregates (and monomers) be negligible but also that  $I_m$  be independent of the precise definition of an aggregate. This requires that the potential of interaction be short-ranged and strongly attractive. The thermal wavelength  $\lambda$  does not play any fundamental role in the above argument except (primarily) as a length scale to keep the above equations dimensionally correct. Any other suitable scaling length might be chosen, *e.g.* the diameter of a molecule ( $\sigma$ ). If we rewrite eqn (A18) and (A19)

$$\rho \sigma^3 = \sum_m \exp(\beta m \mu) \left( \frac{I_m}{m! \sigma^{3m-3}} \right) \quad (\text{A20})$$

$$\exp(-\beta m \mu_m^\circ) = \frac{I_m}{m! \sigma^{3m-3}}, \quad (\text{A21})$$

we will have merely replaced  $\mu$  by  $\mu + kT \ln(\lambda/\sigma)^3$  and  $m \mu_m^\circ$  by  $m \mu_m^\circ + (m-1)kT \ln(\lambda/\sigma)^3$ . That is we have merely changed concentration units and changed the reference state with respect to which the chemical potential is defined. Thus the classical potential of the ideal gas is now  $kT \ln(\rho \sigma^3)$  instead of  $kT \ln(\rho \lambda^3)$ . The reference state is the hypothetical ideal gas of density  $\rho = 1/\sigma^3$ . This change is convenient when working at a fixed temperature but is awkward when considering changes in temperature since the reference state is temperature dependent.

(3) THREE-DIMENSIONAL, MULTICOMPONENT SYSTEMS. The above argument can be extended to a multicomponent system. For example consider an aggregating solute B dissolved in a solvent A. We may write the grand partition function as

$$\exp(\beta PV) = \sum_{N_A} \frac{\exp(\beta N_A \mu_A)}{N_A! \lambda_A^{3N_A}} \sum_{N_B} \frac{\exp(\beta N_B \mu_B)}{N_B! \lambda_B^{3N_B}} \int d^{3N_A} q d^{3N_B} r \exp[-\beta u_{N_A, N_B}(q, r)], \quad (\text{A22})$$

where  $\beta = 1/kT$ ,  $P$  is the pressure,  $V$  the volume,  $\mu_A$  and  $\mu_B$  the chemical potentials of solvent and solute, respectively,  $\lambda_A$  and  $\lambda_B$  the thermal wavelengths and  $u_{N_A, N_B}(q, r)$  the potential energy of the  $N_A$  solvent molecules and  $N_B$  solute

molecules whose positions are given by  $q$  and  $r$ , respectively. If we let  $P_0$  denote the pressure of pure solvent at the given  $\mu_A$  and  $T$  then

$$\exp(\beta P_0 V) = \sum_{N_A} \frac{\exp(\beta N_A \mu_A)}{N_A! \lambda_A^{3N_A}} \int d^{3N_A} \exp[-\beta u_{N_A,0}(q, r)]. \quad (\text{A23})$$

We define the excess free energy  $\bar{u}_{N_B}(r)$  of the  $N_B$  solute molecules as

$$\exp[-\beta \bar{u}_{N_B}(r)] = \exp(-\beta P_0 V) \sum_{N_A} \frac{\exp(\beta N_A \mu_A)}{N_A! \lambda_A^{3N_A}} \int d^{3N_A} q \exp[-\beta u_{N_B, N_A}(q, r)], \quad (\text{A24})$$

so that eqn (A22) may be rewritten as

$$\exp(\beta \pi V) = \sum_{N_B} \frac{\exp(\beta N_B \mu_B)}{N_B! \lambda_B^{3N_B}} \int d^{3N_B} r \exp[-\beta \bar{u}_{N_B}(r)], \quad (\text{A25})$$

where  $\pi = P - P_0$  is the osmotic pressure of the solution relative to pure solvent at pressure  $P$  and temperature  $T$ . Eqn (A25) is completely analogous to eqn (A10) and (A11) with the gas pressure  $P$  replaced by the osmotic pressure  $\pi$  and the potential energy of the gas molecules replaced by the excess free energy of the solute molecules. The same argument may therefore be applied to obtain the law of mass action for the solute and obtain formal expressions for the  $\mu_N^\circ$ . The  $\mu_N^\circ$  are thus given as functions of  $\mu_A$  and  $T$  but for dilute solutions  $\mu_A$  is approximately that of the pure solvent at the appropriate pressure (usually 1 atm).

So far we have only obtained a formal expression for  $\mu_N^\circ$ . In the next subsection we shall attempt to obtain a physical interpretation for  $\mu_N^\circ$ .

(4) PHYSICAL MEANING OF  $\mu_N^\circ$ . We have obtained a formal expression [eqn (A19)] for  $\mu_m^\circ$  in terms of the partition function  $I_m$  defined by eqn (A16). The partition function  $I_m$  resembles a canonical partition function except that for our integral  $I_m$  is over configurations which constitute an aggregate whereas the canonical partition function is an integral over configurations in which the molecules are confined to a fixed volume. However, as is well known in statistical mechanics, the major contribution to the canonical partition function comes from configurations with a uniform density filling the whole container. One might likewise expect that the major contribution to  $I_m$  comes from configurations with a uniform density equal to the average density of an aggregate and that  $I_m$  would be approximately equal to the canonical partition function of a system of  $m$  particles with this average density. The  $m\mu_m^\circ$  would be approximately the Helmholtz free energy of a system of  $m$  molecules of this average density. Since the system is of finite size it will have in addition to a bulk free energy term a surface energy and possibly curvature energy.

It should be clear from the above example that the constraints defining an aggregate should confine the molecules to a sufficiently small volume so that a natural aggregate will form spontaneously just as a gas if confined to a small volume will collapse to form a liquid drop.

The interpretation of  $\mu_m^\circ$  for a solution is more involved. The expression [eqn (A16)] for  $I_m$  will involve the excess free energy defined by eqn (A24). If we assume phase separation of the solute and the solvent then clearly  $m\mu_m^\circ$  equals the bulk Helmholtz free energy for  $m$  molecules at the average aggregate density  $+ P_0 V_{\text{agg}} + \text{surface terms} + \text{curvature terms}$ . If the aggregate is incompressible the sum of the first two terms is the bulk Gibbs free energy of  $m$  molecules at pressure  $P_0$  [i.e. at the external pressure (usually 1 atm) not at the internal pressure of the aggregate which

may differ from  $P_0$  by the Laplace pressure  $2\gamma/r$  where  $\gamma$  is the interfacial tension and  $r$  the radius of curvature of the drop].

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